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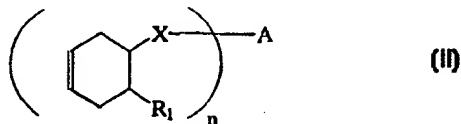
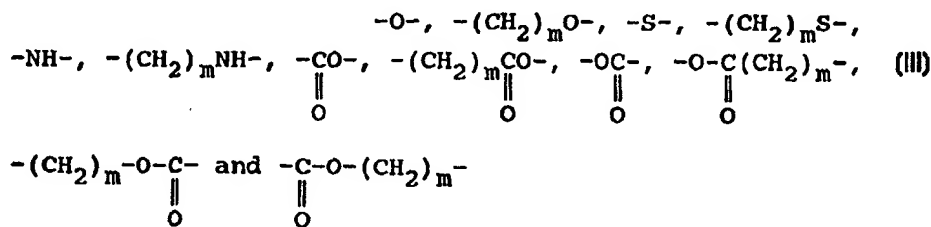
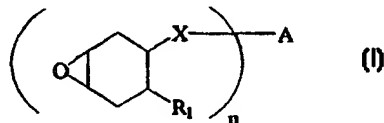
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(21) International Application Number: PCT/EP98/02149 (22) International Filing Date: 9 April 1998 (09.04.98) (30) Priority Data: 08/831,677 10 April 1997 (10.04.97) US (71) Applicant (for all designated States except PL): SARTOMER COMPANY, INC. [US/US]; Oaklands Corporate Center, 502 Thomas Jones Way, Exton, PA 19341 (US). (71) Applicant (for PL only): CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F-92800 Puteaux (FR). (72) Inventors: FAN, Mingxin; 49 Sheffield Lane, West Chester, PA 19380 (US). CESKA, Gary; 310 Long Ridge Lane, Exton, PA 19341 (US). HORGAN, James; 805 Copeland School Road, West Chester, PA 19380 (US). STRUB, Henri; 56, rue de la Chapelle Saint Jean, F-60700 Pont Sainte Maxence (US). (74) Agent: CHAILLOT, Geneviève; Cabinet Chaillot, 16-20, avenue de l'Agent Sarre, Boîte postale 74, F-92703 Colombes Cedex (FR).		(81) Designated States: CA, CN, JP, KR, MX, PL, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>	

(54) Title: CYCLOALIPHATIC EPOXIDES AND THE METHOD FOR MAKING THE SAME



(57) Abstract

Compounds having formula (I) wherein: X is selected from formula (III); m is 1 to 6; n is 1 to 100; R₁ is selected from H, (C₁-C₂₀)alkyl, (C₁-C₂₀) alkoxy and (C₁-C₂₀)ester; and A is a saturated organic group selected from residues of alcohols, polyols, thiols, polythiols, amines, polyamines, acids and polyacids; are prepared by reacting compounds according to formula (II); wherein X, R¹, n and A are as defined above, with hydrogen peroxide in the presence of (a) tungstic acid or its metal salts, (b) phosphoric acid or its metal salts, and (c) at least one phase transfer catalyst.

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CYCLOALIPHATIC EPOXIDES AND THE METHOD FOR MAKING THE SAME.

This invention relates to cycloaliphatic epoxides and an epoxidation process using hydrogen peroxide as oxidizing agent.

5 Recently, a variety of unsaturated polymers have been epoxidized with hydrogen peroxide in the presence of a quaternary ammonium tetrakis (diperoxotungsto) phosphate catalyst (J. Poly. Sci. Part C : Poly. Lett. 1990, 28, 285 ; J. Poly. Sci. : Part A ; Poly. Chem. 1991, 29, 547). This
10 process suffers from certain disadvantages, e.g., the catalyst is not readily available.

Cyclic epoxides are very reactive towards ring opening reactions due to the high ring strain associated with the ring structure, and thus they are very difficult to
15 prepare. Cyclic epoxide precursors are very sensitive to reaction conditions. Currently, these precursors are epoxidized using peracids with careful pH control. Organic acids are used and generated during the epoxidation process.

Cyclic olefins have been epoxidized under phase
20 transfer conditions. However, unsaturated cyclic substrates containing ester or ether linkages are sensitive to side reactions such as cleavage. Epoxidation of these types of substrates under phase transfer conditions has not been demonstrated in the prior art.

25 U.S. Patents 3,360,501 ; 3,023,174 and 2,988,554 and UK specification 907,149, assigned to Ciba Ltd ; and U.S. Patents 2,917,491 ; 2,890,209 ; 2,863,881 ; 2,853,499 ; 2,853,498 ; 2,745,847 and 2,750,395 assigned to Union Carbide Corporation teach processes which can produce cyclic epoxides
30 having up to two cycloaliphatic rings. U.S. Patents 3,671,592 assigned to Nitto Electric Industrial Co. ; and 3,558,665 assigned to Argus Chemical Co. ; and Japanese Kokai 39-2473 of March 10, 1964 assigned to Kanegafuchi Spinning Co., Ltd, also teach processes which can produce cyclic
35 epoxides having only up to two cycloaliphatic rings.

Processes for producing cyclic epoxides having three or more cycloaliphatic rings have not been provided or

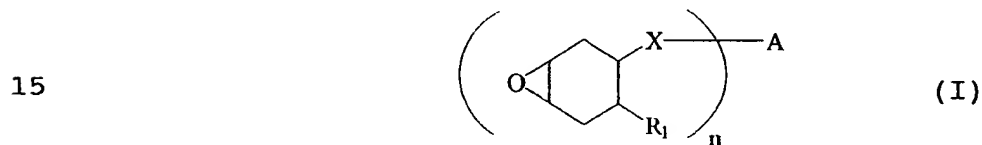
suggested by the prior art.

It is an object of the present invention to eliminate the use of organic acids in the process of epoxidation of cyclic, aliphatic, unsaturated compounds.

5 It is a further object of the invention to simplify the epoxidation process and use hydrogen peroxide directly as epoxidation agent.

A still further object is to provide a new class of cycloaliphatic epoxides having at least three
10 cycloaliphatic rings.

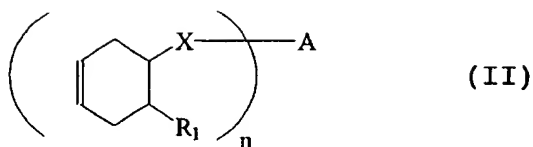
These objects, and others which will become apparent from the following disclosure, are achieved by the present invention which comprises in one aspect a process of preparation of compounds of formula (I) :



wherein :

- 20 - X is selected from -O-, $-(CH_2)_mO-$, -S-, $-(CH_2)_mS-$,
 $-NH-$, $-(CH_2)_mNH-$, $-\overset{\overset{O}{\parallel}}{C}O-$, $-(CH_2)_m\overset{\overset{O}{\parallel}}{C}O-$, $-\overset{\overset{O}{\parallel}}{C}O-$, $-O-\overset{\overset{O}{\parallel}}{C}(CH_2)_m-$,
 $-(CH_2)_m-\overset{\overset{O}{\parallel}}{C}-$ and $-\overset{\overset{O}{\parallel}}{C}-O-(CH_2)_m-$;
- 25 - m is 1 to 6 ;
 - n is 1 to 100 ;
 - R_1 is selected from H, (C_1-C_{20}) alkyl, (C_1-C_{20}) alkoxy and (C_1-C_{20}) ester ; and
 - A is a saturated organic group selected from residues
 30 of alcohols, polyols, thiols, polythiols, amines, polyamines, acids, and polyacids ;
 comprising reacting a compound of formula (II) :

3



wherein X, R₁, n and A are as defined above,
with hydrogen peroxide in the presence of :

- 5 (a) tungstic acid or its metal salts,
- (b) phosphoric acid or its metal salts, and
- (c) at least one phase transfer catalyst.

In another aspect, the invention comprises compounds of formula (I), wherein n is 3 to 100.

- 10 The invention also comprises a process of preparing polymers comprising curing a compound of formula (I) according to the present invention, in the presence of a cationic initiator, it being possible for said curing to be induced by radiation ; and compositions comprising a polymer
- 15 prepared by curing a compound of formula (I) according to the present invention, in the presence of a cationic initiator.

The new method involves low level of catalyst composition and no organic acid and/or peracid, which results in simple product workup and process. The present invention

- 20 uses hydrogen peroxide in the presence of

- (a) tungstic acid or its metal salts,
- (b) phosphoric acid or its metal salts,
- (c) at least one phase transfer catalyst.

The epoxidation of unsaturated cyclic substrates with

- 25 hydrogen peroxide in the presence of tungsten catalyst, phosphoric acid or its salt, and phase transfer catalyst can be performed at any temperature which is sufficient to react, however, particularly suitable temperatures are between about 0°C and 100°C, preferably from about 25°C to 70°C and more
- 30 particularly between about 50 and 70°C. The reaction takes place faster at higher temperature and requires shorter time to complete. The reaction is typically exothermic. Slow addition of hydrogen peroxide is preferred to control the exotherm. The reaction can be performed at pressures from
- 35 subatmospheric to superatmospheric ; however, the reaction is

preferably carried out at atmospheric pressure.

The epoxidation can be performed with or without solvent. Solvent can be used to reduce the viscosity. If solvent is needed, water immiscible organic solvents such as
5 chlorinated hydrocarbons, ethers, glycol ethers, hydrocarbons, combinations thereof, can be used. Particular suitable organic solvents are toluene, chlorobenzene, chloroform, methylene chloride, and the like.

Hydrogen peroxide solution is used as oxidant in
10 the concentration of 5 to 70%. The amount of hydrogen peroxide can vary depending on the desired degree of epoxidation, typically from 0.1 to 1.5 equivalent per unsaturated double bond.

The phase transfer catalyst can be used from about
15 0.001 to 1, preferably about 0.05 to 0.1, equivalents per equivalent of carbon-carbon double bond of compound of formula (II). Suitable phase transfer catalyst includes quaternary ammonium salts, quaternary phosphonium salts, and polyethers ; for example, trioctylmethyl ammonium chloride,
20 trioctylmethyl ammonium bromide, trioctylmethyl ammonium iodide, trioctylmethyl ammonium hydrogen sulfate, trioctylmethyl ammonium nitrate, tetrahexyl ammonium chloride, tetrahexyl ammonium bromide, tetrahexyl ammonium iodide, tetrahexyl ammonium hydrogen sulfate, tetrahexyl
25 ammonium nitrate, tetrabutyl ammonium chloride, tetrabutyl ammonium bromide, tetrabutyl ammonium nitrate, tetrabutyl ammonium hydrogen sulfate, dioctadecyldimethyl ammonium chloride, dioctadecyldimethyl ammonium bromide, dioctadecyldimethyl ammonium nitrate, dioctadecyldimethyl
30 ammonium hydrogen sulfate, dihexadecyldimethyl ammonium chloride, dihexadecyldimethyl ammonium bromide, dihexadecyldimethyl ammonium nitrate, dihexadecyldimethyl ammonium hydrogen sulfate, trioctylmethylphosphonium chloride, trioctylmethylphosphonium bromide,
35 trioctylmethylphosphonium nitrate, trioctylmethylphosphonium hydrogen sulfate, tetrahexylphosphonium chloride, tetrahexylphosphonium bromide, tetrahexylphosphonium nitrate,

tetrahexylphosphonium hydrogen sulfate, tetrabutylphosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium nitrate, tetrabutylphosphonium hydrogen sulfate, tetrabutyl phosphonium iodide, 5 dioctadecyldimethylphosphonium chloride, dioctadecyldimethyl phosphonium bromide, dioctadecyldimethyl phosphonium nitrate, dioctadecyldimethylphosphonium hydrogen sulfate, dihexadecyl dimethylphosphonium chloride, dihexadecyl dimethylphosphonium chloride, dihexadecyldimethylphosphonium bromide, dihexadecyl 10 dimethylphosphonium nitrate, dihexadecyl dimethylphosphonium hydrogen sulfate, tetraalkyl ammonium hydroxide, tetraalkyl ammonium tribromide, tetraalkyl ammonium trifluoromethane sulfonate, polyethyleneglycol, polypropyleneglycol, polyethylene glycol-polypropylene glycol copolymer, any 15 combination thereof and the like.

Phosphoric acid or its various salts can be used from 0.001 to 0.5 equivalents per equivalent of carbon-carbon double bond of compound of formula (II). Sodium or potassium salts of monobasic, dibasic, or tribasic salts of phosphoric 20 acid can also be used. The final pH can be adjusted by other acids or bases to about 0-5.

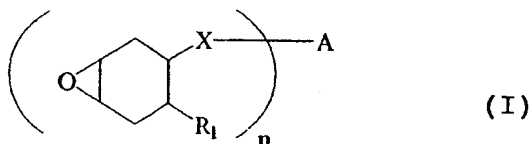
Tungsten catalysts can be used from 0.001 to 50% by weight based on the cyclic substrates. Tungstic acid or its metal salts can be used as the metal catalysts, the metal 25 salts are water soluble and the acid is not. The typical catalyst is used from about 0.005 to 1% and the preferred catalyst is tungstic acid which is not water soluble. Molybdenum derivatives may be used instead of tungsten compounds. Either tungstic acid which is not water soluble 30 or its metal salts which are soluble can be used as the metal catalyst. The typical catalyst is used in amounts of about 0.005 to 1%, based on weight of unsaturated compound of formula (II). The preferred metal catalyst is tungstic acid.

The epoxidation can be performed with or without 35 solvent. The use of solvent is preferred because it reduces the viscosity. If solvent is desired, a water immiscible organic solvent such as chlorinated hydrocarbons, and ethers,

glycol ethers, hydrocarbons, and combinations thereof, are especially useful. Particularly suitable organic solvents are toluene, chlorobenzene, chloroform, methylene chloride, heptane, and the like.

5 The method of the invention allows use of a low level of catalyst composition free of organic acid and/or peracid, resulting in simple product workup and process, and using readily available catalysts.

The new class of cyclic epoxides have the general
10 formula :



wherein :

- X is selected from -O-, $-(CH_2)_mO-$, -S-, $-(CH_2)_mS-$,
15 -NH-, $-(CH_2)_mNH-$, $-\overset{\overset{O}{\parallel}}{CO}-$, $-(CH_2)_m\overset{\overset{O}{\parallel}}{CO}-$, $-\overset{\overset{O}{\parallel}}{OC}-$, $-O-\overset{\overset{O}{\parallel}}{C}(CH_2)_m-$,
 $-(CH_2)_m-\overset{\overset{O}{\parallel}}{O}-\overset{\overset{O}{\parallel}}{C}-$ and $-\overset{\overset{O}{\parallel}}{C}-O-(CH_2)_m-$;
20

- m is 1 to 6 ;
- n is 3 to 100 ;
- R_1 is (C_1-C_{20}) ester ; and
- A is a saturated organic group selected from residues of
25 polyols, polythiols, polyamines and polyacids.

Suitable organic linking groups A in the case of the process are selected from residues of alcohols, polyols, thiols, polythiols, amines, polyamines, acids, and polyacids. Suitable alcohols include methanol, ethanol, propanol, and
30 the like, up to C_{18} alcohols including their alkoxyated derivatives. Suitable polyols include, for example, 1,4-butane diol, 1,6-hexane diol, trimethylpropane, pentaerythritol including their alkoxyated derivatives like ethoxyated and propoxyated trimethylolpropane or
35 pentaerythritol, polyvinyl alcohol, dipentaerythritol and OH-

functional polyesters or acrylic oligomers. Suitable acids include, for example, acrylic and methacrylic acid, whereas suitable polyacids include, for example, succinic acid, adipic acid, polyacrylic acid and copolymers thereof or
 5 carboxy functional polyesters. Examples of amines include monoethanol amine, butylamine, diethyl amine, diethanolamine, and the like. Examples of thiols are the thiol analogues of the alcohols and polyols.

In the case of the compounds, where n is 3 to 100,
 10 suitable organic linking groups, A, are selected from residues of polyols, polythiols, polyamines, and polyacids having a functionality of 3 to 100. Lists of particular polyols, polythiols, polyamines and polyacids are recited in the abovementioned paragraph.

15 Preferred A has up to 36 carbon atoms. More particularly, A may be selected from residues of (C₃-C₂₀)alkylene triols, trithiols, triamines and triacids.

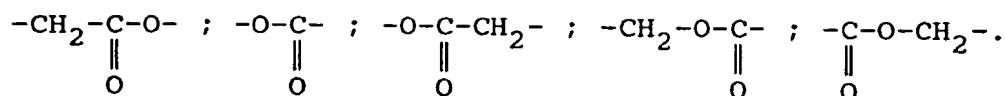
Concerning the process, suitable (C₁-C₂₀) alkyl groups for R₁ are methyl, ethyl, propyl, butyl, and the
 20 like, with butyl preferred ; and suitable (C₁-C₂₀) alkoxy groups for R₁ are methoxy, ethoxy, and the like, and alkoxyated alkoxy groups.

Concerning the compounds and the process, suitable (C₁-C₂₀) ester groups are preferably ester group of the
 25 formula -COOR₂, wherein R₂ is selected from the group consisting of (C₁-C₂₀) alkyl, such as methyl, ethyl, propyl, butyl and the like.

X is selected from -O-, -(CH₂)_mO-, -S-, -(CH₂)_mS-,
 30 -NH-, -(CH₂)_mNH-, $\begin{array}{c} \text{O} \\ \parallel \\ \text{-CO-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{-(CH}_2\text{)}_m\text{C-O-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{-OC-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{-OC(CH}_2\text{)}_m\text{-} \end{array}$,

$\begin{array}{c} \text{O} \\ \parallel \\ \text{-(CH}_2\text{)}_m\text{-O-C-} \end{array}$ and $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-O-(CH}_2\text{)}_m\text{-} \end{array}$; wherein m is 1 to 6. The

35 most preferred X groups are -O- ; -CH₂-O- ; $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-O-} \end{array}$;



In the product of the process of the invention defined by
 5 formula (I), whenever n is 2 or more, each X can be different, but is preferably the same.

n may be 3 to 5 ; diepoxides, wherein n is 2, are preferred in the case of the process, A being the residue of a polyol, a polythiol, a polyamine or a polyacid ;
 10 triepoxydes, wherein n is 3, are preferred in the case of the compounds.

As examples of compounds according to the present invention, compounds wherein :

- n is 3 ;
- 15 - R_1 is a (C_1 - C_{20}) ester group ; and
- X is $-\text{CO}-$ or $-\text{OC}-$ or $-\text{CH}_2-\text{C}-\text{O}-$ or $-\text{O}-\text{C}-\text{CH}_2-$ or
 \parallel \parallel \parallel \parallel
 O O O O
- 20 $-\text{CH}_2-\text{O}-\text{C}-$ or $-\text{C}-\text{O}-\text{CH}_2-$;
 \parallel \parallel
 O O

and compounds wherein :

- X is $-\text{CO}-$;
 \parallel
 O
- 25
- n is 3 ;
- R_1 is an ester group of formula $-\text{COOR}_2$ wherein R_2 is butyl ; and
- A is the residue of trimethylolpropane
- 30 can be cited.

The novel cyclic epoxides produced by the process of the invention can be used in applications such as coatings, epoxy / amine cure, cationic cure, and chemical intermediates for functionalizations.

35 A particular embodiment of the invention concerns cationically curable compositions comprising compounds of formula (I). More particularly, the invention concerns

cationically curable compositions comprising compounds of formula (I) wherein the curing can be induced by UV radiation in the presence of a suitable cationic photoinitiator, selected for example from aryldiazonium salts, diaryliodonium salts or sulphonium salts and preferably from hexafluorophosphates or hexafluoroantimonates of these salts. Finally, the invention concerns cured coating compositions obtained by curing these compositions either by general cationic cure or by specific UV cationic cure.

10 The following non-limiting examples are presented to illustrate a few embodiments of the invention. All parts and percentages are by weight unless otherwise indicated.

Example 1

Preparation of Ethylenically Unsaturated Diester

15 Tetrahydrophthalic anhydride (152.2 g), 1-butanol (74.1 g) were added to the reactor and the mixture was heated while stirring to 110°C. Exothermic reaction took place and the reactor temperature reached to 150°C. Water cooling was applied to control the temperature at 110°C. The reaction
20 was kept at 110°C for two hours when the acid anhydride absorption disappeared based on FTIR. Tetrahydrophthalic anhydride butyl half ester was obtained.

 After cooling, 1,4-butanediol (46.0 g), toluene (60.0 g), heptane (60.0 g), and methane sulfonic acid (70%,
25 8.0 g) were added, the mixture was stirred and heated to reflux. Esterification took place and the water formed was removed azeotropically ; esterification was completed in three hours and 20.2 grams of water was collected. The reaction mixture, after cooling down to room temperature, was
30 washed with 25.0 g of 25% sodium hydroxide twice. The final product was isolated by removing the solvents under reduced pressure (yield : 205.0 g).

Example 2Preparation of Diepoxide from Unsaturated Diester

Product from Example 1 (100.0 g) was added to a reactor, followed by tungstic acid (0.80 g), phosphoric acid (85%, 0.40 g), sodium hydroxide (25%, 0.40 g), Aliquot 336 (0.80 g) and toluene (200.0 g). The mixture was stirred and heated to 50°C when slow addition of hydrogen peroxide (30%, 65.0 ml) began. The hydrogen peroxide addition was completed in 70 minutes to control the exotherm. The reaction mixture was kept at 50°C for 2.5 additional hours when no residual starting material was detected by GC and FTIR.

The final mixture was separated into two phases. The organic phase was isolated and washed twice with 50 ml of water to remove the excess hydrogen peroxide. The final dicycloaliphatic epoxide was isolated by removing solvent at 95°C under reduced pressure which has epoxy equivalent weight of 280.1 g/eq (yield : 94.0 g).

Example 3Preparation of Unsaturated Dicyclic Diester

6-Methyl-3-cyclohexene-1-1-methanol (180.0 g), adipic acid (100.0 g), heptane (120.0 g), and methanesulfonic acid (70%, 6.0 g) were added to a reactor which was equipped with a mechanical stirrer, condenser, thermal couple. The reaction mixture was heated to reflux under stirring and esterification process took place. The water formed was removed azeotropically while refluxing. The reaction was completed in 6 hours and the final temperature was 110°C ; 26.6 grams of water was collected.

The final reaction mixture was washed with 10.0 g of 25% sodium hydroxide after cooling down to room temperature. The final dicyclic diester was isolated by removing the heptane solvent at 95°C under reduced pressure (yield : 237.0 g).

Example 4Preparation of Diepoxide from Unsaturated Dicyclic Diester

Unsaturated dicyclic diester from Example 3 (100.0 g) was added to a reactor, followed by tungstic acid (0.80 g), phosphoric acid (85%, 0.40 g), sodium hydroxide (25%, 0.40), Aliquot 336 (0.80 g), and toluene (200.0 g). The mixture was stirred and heated to 50°C when slow addition of hydrogen peroxide (30%, 70.0 ml) began. The hydrogen peroxide addition was completed in 40 min to control the exotherm. The reaction mixture was kept at 50°C for 2.0 additional hours when no residual starting material was detected by GC and FTIR.

The final mixture was separated into two phases, the organic phase was isolated and washed twice with 50 ml of water to remove the excess hydrogen peroxide. The final dicycloaliphatic epoxide was isolated by removing solvent at 95°C under reduced pressure which has epoxy equivalent weight of 207.0 g/eq (yield : 105.5 g).

Example 5Preparation of Esters

Tetrahydrophthalic anhydride (152.2 g) and 1-butanol (74.1 g) were added to the reactor, the mixture was heated while stirring to 110°C. Exothermic reaction took place and the reactor temperature reached to 150°C, and then water cooling was applied and the temperature was controlled at 110°C. The reaction was kept at 110°C for two hours when the acid anhydride absorption disappeared based on FTIR.

After cooling, trimethylolpropane (44.7 g), heptane (110.0 g), and methane sulfonic acid (70%, 8.0 g) were added. The mixture was then stirred and heated to reflux. Esterification took place and the water formed was removed azeotropically. Esterification completed in three hours and 19.43 grams of water was collected. The reaction mixture, after cooling down to room temperature, was washed with

25.0 g of 25% sodium hydroxide twice. The final product was isolated by removing the solvents under reduced pressure (yield : 235.0 g).

Example 6

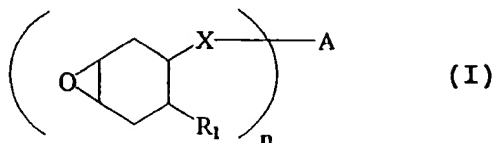
5 Preparation of triepoxides

The product from Example 5 (172.0 g) was added to a reactor, followed by tungstic acid (1.43 g), phosphoric acid (85%, 0.70 g), sodium hydroxide (25%, 0.70 g), Aliquat 336 (1.41 g), and toluene (300.0 g). The mixture was stirred
10 and heated to 60°C when slow addition of hydrogen peroxide (30%, 100.0 ml) was begun. The hydrogen peroxide addition was completed in 70 min to control the exotherm. The reaction mixture was kept at 60°C for 12.0 additional hours after which no residual starting material was detected by GC
15 and FTIR. The final mixture was separated into two phases. The organic phase was isolated and washed twice with 50 ml of water to remove the excess hydrogen peroxide. The final tricycloaliphatic epoxide product was isolated by removing solvent at 70°C under reduced pressure. The product had an
20 epoxy equivalent weight of 350.0 g/eq (yield : 146.3 g).

While the invention has been described in sufficient detail for those skilled in the art to make and use it, various modifications, alternatives, and improvements should become readily apparent without departing from the
25 spirit and scope of the invention as set forth in the following claims.

CLAIMS

1 - Compounds of the formula (I) :



wherein :

- 5 - X is selected from $-O-$, $-(CH_2)_mO-$, $-S-$, $-(CH_2)_mS-$, $-NH-$, $-(CH_2)_mNH-$, $-\overset{\overset{O}{\parallel}}{C}-$, $-(CH_2)_m\overset{\overset{O}{\parallel}}{C}O-$, $-\overset{\overset{O}{\parallel}}{C}-$, $-O-\overset{\overset{O}{\parallel}}{C}(CH_2)_m-$, $-(CH_2)_m-O-\overset{\overset{O}{\parallel}}{C}-$ and $-\overset{\overset{O}{\parallel}}{C}-O-(CH_2)_m-$;
- 10 $-\overset{\overset{O}{\parallel}}{C}-O-(CH_2)_m-$ and $-(CH_2)_m-O-\overset{\overset{O}{\parallel}}{C}-$;
- m is 1 to 6 ;
 - n is 3 to 100 ;
 - R_1 is (C_1-C_{20}) ester ; and
- 15 - A is a saturated organic group selected from residues of polyols, polythiols, polyamines, and polyacids.
- 2 - Compounds according to claim 1 wherein R_1 is an ester group of the formula $-COOR_2$ wherein R_2 is selected from the group consisting of (C_1-C_{20}) alkyl.
- 20 3 - Compounds according to claim 1 or 2 wherein A has up to 36 carbon atoms, more particularly being selected from residues of (C_3-C_{20}) alkylene triols, trithiols, triamines, and triacids.
- 4 - Compounds according to claim 1 or 2 wherein n
- 25 is 3 to 5, more particularly 3.
- 5 - Compounds according to anyone of claims 1 to 4 wherein X is $-O-$; $-CH_2-O-$; $-\overset{\overset{O}{\parallel}}{C}-O-$; $-CH_2-\overset{\overset{O}{\parallel}}{C}-O-$; $-O-\overset{\overset{O}{\parallel}}{C}-$; $-O-\overset{\overset{O}{\parallel}}{C}-CH_2-$; $-CH_2-O-\overset{\overset{O}{\parallel}}{C}-$; $-\overset{\overset{O}{\parallel}}{C}-O-CH_2-$.
- 30 $-O-\overset{\overset{O}{\parallel}}{C}-CH_2-$; $-CH_2-O-\overset{\overset{O}{\parallel}}{C}-$; $-\overset{\overset{O}{\parallel}}{C}-O-CH_2-$.

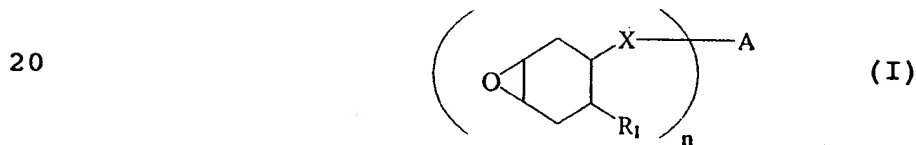
6 - Compounds according to claim 1 or 2 wherein :

- n is 3 ;
- R_1 is a (C_1-C_{20}) ester group ; and
- X is $\begin{array}{c} \text{-CO-} \\ \parallel \\ \text{O} \end{array}$ or $\begin{array}{c} \text{-OC-} \\ \parallel \\ \text{O} \end{array}$ or $\begin{array}{c} \text{-CH}_2\text{-C-O-} \\ \parallel \\ \text{O} \end{array}$ or $\begin{array}{c} \text{-O-C-CH}_2\text{-} \\ \parallel \\ \text{O} \end{array}$ or
 $\begin{array}{c} \text{-CH}_2\text{-O-C-} \\ \parallel \\ \text{O} \end{array}$ or $\begin{array}{c} \text{-C-O-CH}_2\text{-} \\ \parallel \\ \text{O} \end{array}$.

7 - Compounds according to claim 1 or 2 wherein :

- X is $\begin{array}{c} \text{-CO-} \\ \parallel \\ \text{O} \end{array}$;
- n is 3 ;
- R_1 is an ester group of formula $-\text{COOR}_2$ wherein R_2 is butyl ; and
- A is the residue of trimethylolpropane.

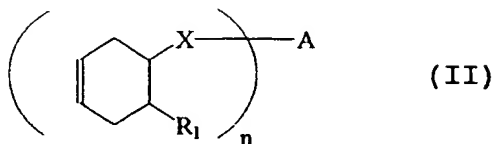
8 - Process of preparation of compounds of formula (I) :



wherein :

- X is selected from $-\text{O}-$, $-(\text{CH}_2)_m\text{O}-$, $-\text{S}-$, $-(\text{CH}_2)_m\text{S}-$,
 $-\text{NH}-$, $-(\text{CH}_2)_m\text{NH}-$, $\begin{array}{c} \text{-CO-} \\ \parallel \\ \text{O} \end{array}$, $\begin{array}{c} \text{-(CH}_2\text{)}_m\text{CO-} \\ \parallel \\ \text{O} \end{array}$, $\begin{array}{c} \text{-OC-} \\ \parallel \\ \text{O} \end{array}$, $\begin{array}{c} \text{-O-C(CH}_2\text{)}_m\text{-} \\ \parallel \\ \text{O} \end{array}$,
 $\begin{array}{c} \text{-(CH}_2\text{)}_m\text{-O-C-} \\ \parallel \\ \text{O} \end{array}$ and $\begin{array}{c} \text{-C-O-(CH}_2\text{)}_m\text{-} \\ \parallel \\ \text{O} \end{array}$;
- m is 1 to 6 ;
- n is 1 to 100 ;
- R_1 is selected from H, (C_1-C_{20}) alkyl, (C_1-C_{20}) alkoxy and (C_1-C_{20}) ester ; and
- A is a saturated organic group selected from residues of alcohols, polyols, thiols, polythiols, amines, polyamines, acids, and polyacids ;

comprising reacting a compound of formula (II) :



wherein X, R¹, n and A are as defined above,
with hydrogen peroxide in the presence of

- 5 (a) tungstic acid or its metal salts,
- (b) phosphoric acid or its metal salts, and
- (c) at least one phase transfer catalyst.

9 - Process according to claim 8 wherein said n is
2 to 100 and A is a residue of a polyol, polythiol, polyamine
10 or polyacid.

10 - Process according to claim 8 or 9 wherein said
hydrogen peroxide is introduced in an amount of about 0.1 to
1.5 equivalent per equivalent of unsaturated double bond in
the compound of formula (II).

15 11 - Process according to anyone of claims 8 to 10
wherein the reacting is conducted at a temperature of about
0°C to 100°C, preferably of about 25°C to 70°C and more
particularly of about 50 to 70°C.

12 - Process according to anyone of claims 8 to 11
20 wherein the phase transfer catalyst is present in an amount
of about 0.001 to 1 equivalents, particularly in an amount of
about 0.05 to 0.1 equivalents, per equivalent of carbon-
carbon double bond in the unsaturated compound of formula
(II).

25 13 - Process according to anyone of claims 8 to 12
wherein the phase transfer catalyst is selected from the
group consisting of quaternary ammonium salts, quaternary
phosphonium salts, and polyethers.

14 - Process according to anyone of claims 8 to 13
30 wherein the reaction is conducted in the presence of a water
immiscible organic solvent, in particular selected from the
group consisting of chlorinated hydrocarbons, ethers, glycol
ethers, hydrocarbons, combinations thereof, such as toluene,

chlorobenzene, chloroform, methylene chloride and heptane.

15 - Process according to anyone of claims 8 to 14 wherein the phosphoric acid or phosphoric acid salt comprises about 0.001 to 0.5 equivalents per equivalent of carbon-
5 carbon double bond of the compound of formula (II).

16 - Process according to anyone of claims 8 to 15 wherein the phosphoric acid or salt thereof is a sodium or potassium salt of monobasic, dibasic, or tribasic phosphoric acid.

10 17 - Process according to anyone of claims 8 to 16 wherein the pH of the reaction is adjusted by acid or base to about 0-5.

18 - Process according to anyone of claims 8 to 17 wherein the tungstic acid or salts thereof is tungstic acid.

15 19 - Process according to anyone of claims 8 to 18 wherein the tungstic acid or salts thereof is present in an amount of about 0.005 to 1% based on weight of compound of formula (II).

20 20 - Process of preparing polymers comprising curing a compound of formula (I) as defined in anyone of claims 1 to 7 in the presence of a cationic initiator.

21 - Process according to claim 20 wherein said curing is induced by radiation.

25 22 - Composition comprising a polymer prepared by curing a compound of formula (I) as defined in anyone of claims 1 to 7 in the presence of a cationic initiator.

30 23 - Cationically curable coating composition, in particular UV radiation curable composition comprising a compound of formula (I) as defined in anyone of claims 1 to 7.

24 - Cured coating composition obtained by curing a composition as defined in claim 23.